Melt electrospinning towards industrial scale nanofiber production

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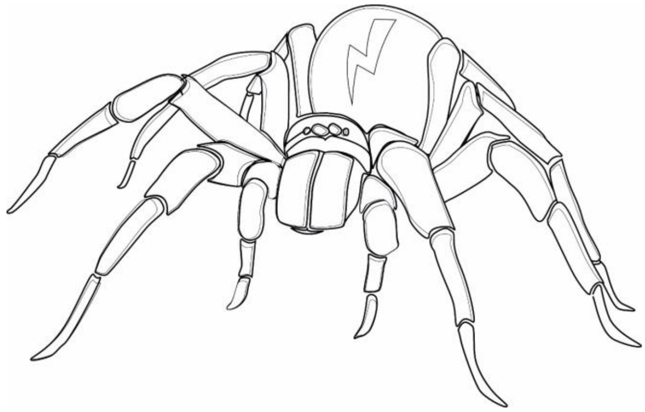
Chapter 6

Valorization



Valorization

The unique properties of nanofibers, such as high flexibility and an enormous specific surface area, making them suitable for applications in various fields such as medicine, energy and electronics, filtration and separation, and the manufacture of textiles, have significantly increased research interest in efficient nanofiber manufacturing processes [1]. Nevertheless, a key challenge for industry is the ability to upscale nanofiber production. Several methods, as described in **Chapter 1**, can be used to produce nanofibers and sub-microfibers, but melt electrospinning is among the most promising technologies in terms of fiber structure and the breadth of downstream applications due to the absence of solvents in the manufacturing process [2]. The major drawback of melt electrospinning is its low throughput, resulting in the adoption of solution electrospinning as the prevailing industrial process technology. Recent device developments such as multiple needle and needleless configurations have demonstrated a roadmap to overcome the low throughput in melt electrospinning, although an industrial process has yet to be established [3]. In this thesis, a new developed scaled-up melt-electrospinning prototype featuring 600 nozzles, bridging the gap between laboratory-scale and industrial-scale nanofiber manufacturing, has been presented. The prototype device vastly exceeds the capabilities of any state-of-the-art technology and has been successfully used to produce nanofibers with the same quality and properties compared to nanofibers produced with the more conventional solution electrospinning process.

In addition, we were able to make a decisive contribution to the still necessary material development for melt-electrospinable polymers [3, 4] based on polypropylene (**Chapter 3**) and the biobased polymer polylactic acid (**Chapter 4**). With the approach of adding additives such as salts like sodium stearate, oleate and chloride as well as the biobased dyed alizarin, hematoxylin and quercetin in combination with plasticizers [5], we were able to overcome the obstacles of poor polymer conductivity and insufficient viscosity of the initial polymers, thus successfully approaching fiber production in the sub-micro range [2]. For the first time, the correlation between spin pump speed, temperature/viscosity and additive concentration/conductivity on the reduction of the fiber diameter could be statistically validated for a pilot-scale melt-electrospinning device using SPSS two-way analysis of variance [2]. This validation will facilitate further material development, as basic principles such as a decrease in fiber diameter with decreasing viscosity and decreasing spin pump speed, can be assumed to be known. Thus, it is possible to focus on the investigation of the polymer melt conductivity in order to achieve a classification of melt-electrospinable polymers. By introducing the climate control system in the form of a glass chamber (**Chapter 5**), fiber diameters, which are comparable to those produced by conventional solution electrospinning, could be achieved, thereby emphasizing the innovative performance of the prototype.

For a better comprehension of the fiber diameter dimensions achieved in this thesis, the fiber diameters produced with the pilot-scale melt-electrospinning device have been related to the fiber diameters depending on the nanofiber production methods described in **Chapter 1** (Figure 6.1).

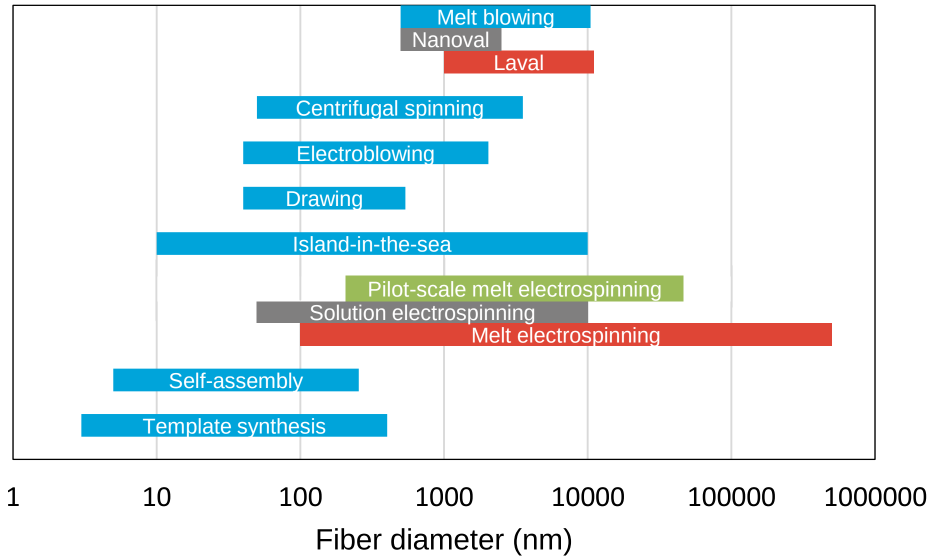


Fig. 6.1: Fiber diameters obtained from pilot-scale melt electrospinning compared to other production methods.

It has to be taken into account that most melt-electrospun sub-microfibres are produced using small devices that are not suitable for sustainable, industrial production [3, 6, 7]. For a multi-nozzle melt-electrospinning device with 600 nozzles, as presented in this thesis, the average fiber diameter of 810 nm and single fiber diameter of 420 nm is the smallest fiber diameter achieved so far.

In the following, the utilization of the novel prototype melt-electrospinning device will be evaluated based on two product examples with industrial relevance, which are currently manufactured using the solvent electrospinning process. The aim is to show that the current production process can be advantageously replaced by melt electrospinning. The two examples considered here are nanofibers for air filtration, as well as nanofiber scaffolds as medical product.

Hardly any other topic has gained so much attention in Central Europe in the recent past as environmentally friendly road transport due to the high level of air pollution especially inside big cities. The biggest public debate was triggered by the "diesel scandal". Increased car exhaust emission levels have been observed in various diesel models. Highly efficient surface filters could be a key technology for solving this problem. An important feature of filter materials is their specific surface. Figure 6.2 shows the relationship between the specific surface area and the diameter of the fibers. As the fiber diameter increases, the specific surface area decreases. Conversely, the smaller the fiber, the larger the specific surface area.

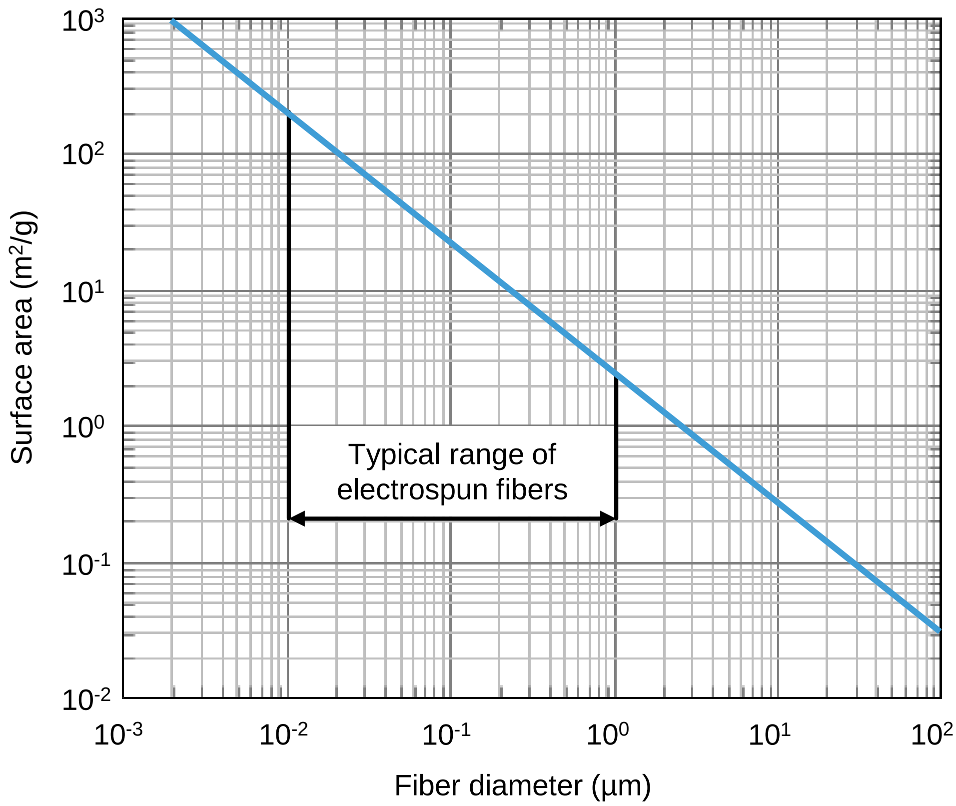


Fig. 6.2: Relationship between the specific surface area and the diameter of fibers.

Nanofibers with their large surface area per fiber mass and simultaneously high porosity improve filter performance and naturally occurring nanoparticles such as viruses and microscopic particles such as bacteria and fine dust can be filtered [8]. Already in 1965, Paul Dutch investigated the influence of fiber diameter on the ability to separate particles of different sizes in an air stream. It could be shown that the binding forces between fiber and dirt particles are always maximal when the diameters of fiber and particles are about the same size [9]. In addition to the separation efficiency, a filter medium is also characterized by its pressure drop. In the world of nanofibers and nanoparticles, physical effects occur which positively influence the flow resistance of these filter media. Considering the behaviour of air that can be observed while flowing around a microfiber, the flow velocity directly at the surface of the fiber is zero, which results in a correspondingly high flow resistance. For fibers with diameters smaller than 500 nm, the so-called slip-flow effect occurs, which ensures that the flow velocity does not drop to zero at the surface for such small fibers, resulting in a comparatively low flow resistance [10]. This is of crucial importance for the filter industry, since instead of increasing flow resistance by increasing the surface area, flow resistance is reduced by increasing the surface area by using nanofibres.

MANN+HUMMEL (Ludwigsburg, Germany) developed nanofiber coated filter media for highly efficient particle separation, even of fine particles below one micrometer. These filter media are characterized by demonstrably higher separation efficiency with a high dust holding capacity. With diameters below one micrometer, these filter-coating fibers, produced using the solvent electrospinning process, are much smaller than the 10-30 µm thick carrier fibers (Figure 6.3) [11].

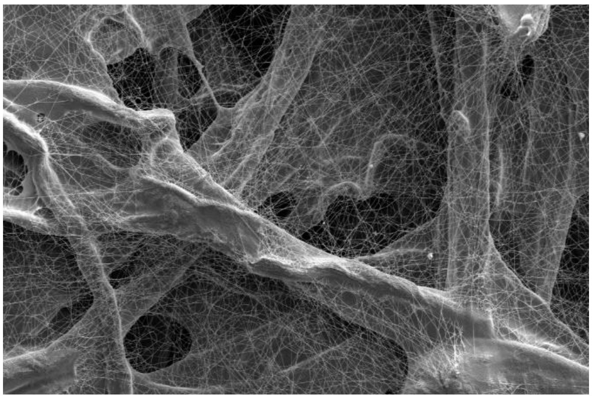


Fig. 6.3: MANN+Hummel filter-coating fibers on carrier material.

The comparison of the nanofiber filter medium with the pure carrier material shows the efficiency of nanofiber technology in filtering. In tests of filter elements according to standard ISO 5011, the nanofiber filter medium achieves up to 10 times less dust passage compared to the pure carrier material. Standard cellulose media enable the separation of 99.9% of the total mass of dust particles from the air. The close-meshed nanofiber layers increase the so-called separation efficiency to up to 99.99% [11]. Furthermore, the service life of such filter elements with their fabric-like nanofiber technology is two times longer than that of conventional filter media, which offers a considerable high potential for cost savings [8].

With our lowest average fiber diameter of 810 nm achieved using the 600-nozzle melt-electrospinning device (**Chapter 5**), we meet the requirements for the fiber diameters of less than 1 µm needed for the filter coating and can directly substitute the previously used manufacturing process. This is desirable from an economic and environmental point of view because only 2–10% of the liquid processed during solution electrospinning is the polymer (the rest is solvent that evaporates) whereas 100% of the processed liquid solidifies into fibers during melt electrospinning [1]. In **Chapter 4** we were able to show that a process change from solution to melt electrospinning leads to a cost reduction of 99.7% in the first production cycle if only material costs are considered and no solvent recovery step is taken into account. The cost reduction results primarily from the absence of expensive solvents such as chloroform with a price of 1000 euro/kg. For the production of 1 kg of PLA fibers, 97% of the material costs can be saved from the second production cycle onwards compared to solution electrospinning with an estimated solution recovery of 90% [5].

Not only the filtration industry benefits from the use of nanofibers. Nanofibers from polylactic acid, an environmentally friendly and biodegradable polymer, are usually prepared by solvent electrospinning using dichloromethane, chloroform or *N,N*-dimethylformamide [2]. Besides the high cost for the solvents and the elaborate solvent recovery process, as described above, the potential carryover of toxic solvents into the final product raises an additional risk for biomedical applications (**Chapter 4**) [4].

DiPole Materials (Baltimore, United States) produces solution-electrospun BioPapers. BioPapers are nanofiber cell scaffolds composed of biologically-derived materials that create a cell microenvironment for drug screening, 3D bioprinting or tissue engineering [12]. Electrospun nanofiber nonwovens are structurally similar to the human extracellular matrix and thus promote successful cell growth [12]. Available are PLA scaffolds as 6 mm discs with a fiber diameter of approx. 650 nm, randomly aligned with a pore size between 1-15 µm. When changing for the melt-electrospinning process, a toxicity of the materials caused by solvent residues can be excluded [2]. The product required fiber diameters are a little smaller than the previously achieved smallest average fiber diameter of 810 nm. Nevertheless, single fiber diameters of 420 nm have already been produced with the prototype melt-electrospinning device. Further increasing the temperature slightly and therewith reducing the material viscosity or reducing the spin pump speed can further reduce the average fiber diameter.

The increasing environmental awareness of the population and the resulting political goals are obliging the industry more and more to deal with the production of sustainable products. If existing product materials can be replaced by biobased polymers such as PLA, the production methods have also to be adapted sustainably. The presented upscaled melt-electrospinning process for the manufacture of microscale and nanoscale fibers prevents the use and disposal of toxic solvents, as well as a possible carry-over of the solvent into the final product, making a decisive contribution to a truly sustainable process chain. It could thus be shown that the device technology developed can be used advantageously compared to previous processes for the manufacture of actual industrially relevant product examples. Furthermore, the prototype melt-electrospinning device can serve as a model for a further scaling up in order to produce large-scale nonwovens with a width of more than actual 34 cm.

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